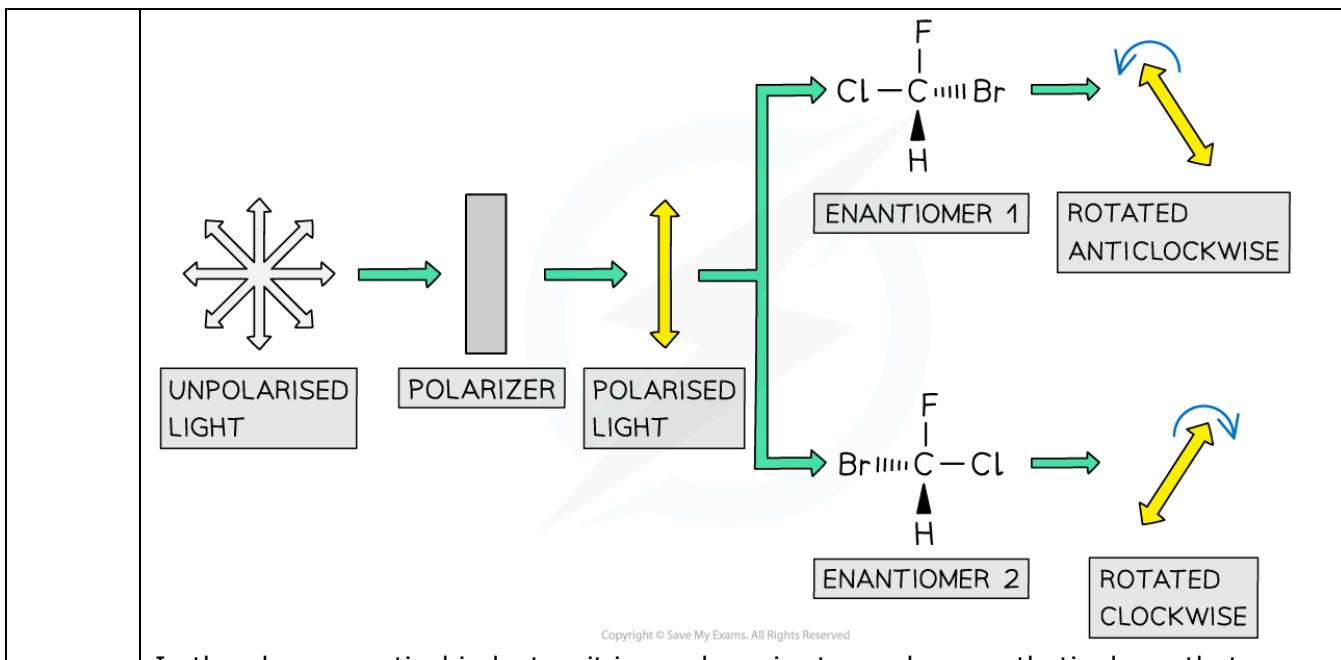


Topic 15: Organic Chemistry: Carbonyls, Carboxylic Acids and Chirality

15A: Chirality

Students will be assessed on their ability to:

15.1	know that optical isomerism is a result of chirality in molecules with a single chiral centre
	In stereoisomerism, molecules have the same molecular and structural formula but they have different arrangements of atoms and groups of atoms in 3 dimensions Optical isomerism is a form of stereoisomerism that occurs due to chirality in molecules with a single chiral centre Optical isomerism occurs in carbon compounds with 4 different groups of atoms attached to a carbon
15.2	understand that optical isomerism results from chiral centre(s) in a molecule with asymmetric carbon atom(s) and that optical isomers (enantiomers) are object and non-superimposable mirror images and be able to draw 3D diagrams of these optical isomers
	A carbon atom that has 4 different atoms or groups of atoms attached to it is called a chiral centre (it is asymmetric) Compounds with one chiral centre exist as two optical isomers, known as enantiomers Enantiomers (optical isomers) are non-superimposable mirror images of each other but are otherwise the same When there are two chiral centres in a compound, there are 4 optical isomers When there are three chiral centres in a compound, there are 8 stereoisomers Number of (optical) isomers = 2^n where n is the number of chiral centres
15.3	know that optical activity is the ability of a single optical isomer to rotate the plane of polarisation of plane-polarised monochromatic light in molecules containing a single chiral centre
	Optical activity is the ability of a single optical isomer to rotate the plane of polarisation of plane-polarised monochromatic light in molecules containing a single chiral centre Optical isomers have identical physical properties, but they only differ by the way they interact with plane-polarised light (i.e. the way they rotate plane-polarised light by equal angles in opposite directions, one rotates +60, the other -60) Optical isomers have identical chemical properties, but they only differ by the way they interact with other chiral molecules (this chemical property may be different for each enantiomer)
15.4	know what is meant by the term 'racemic mixture'
	Racemic mixture (or racemate) is a mixture containing equal amounts (50/50) of each enantiomer, meaning that it has no optical activity One enantiomer rotates the plane of plane-polarised light clockwise (+)(dextrorotatory), the other rotates light anticlockwise (-)(laevorotatory) and as such, the enantiomers cancel each other out which results in it having no optical activity (i.e. the plane of polarization will not change)



In the pharmaceutical industry, it is much easier to produce synthetic drugs that are racemic mixtures than producing one enantiomer of the drug

15.5 be able to use data on optical activity of reactants and products as evidence for S_N1 and S_N2 mechanisms and addition to carbonyl compounds

In unimolecular, there is only one species reacting in the rate determining step
In bimolecular, there are two species reacting in the rate determining step

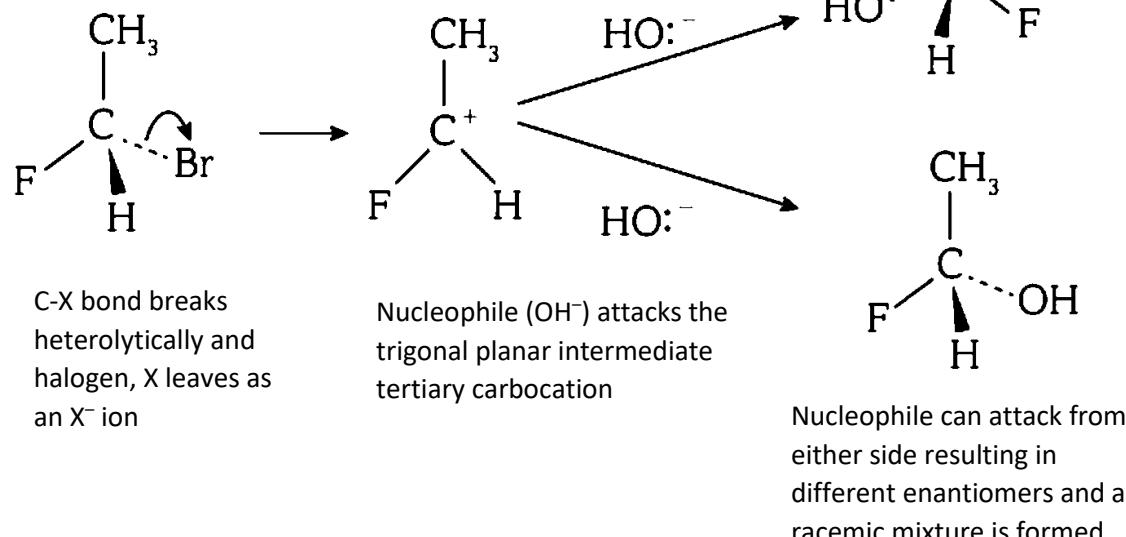
We can know the mechanism of a reaction by measuring the original reactant's optical activity and the product formed

Nucleophilic substitution can occur via an S_N1 or S_N2 mechanism

S_N1 mechanism

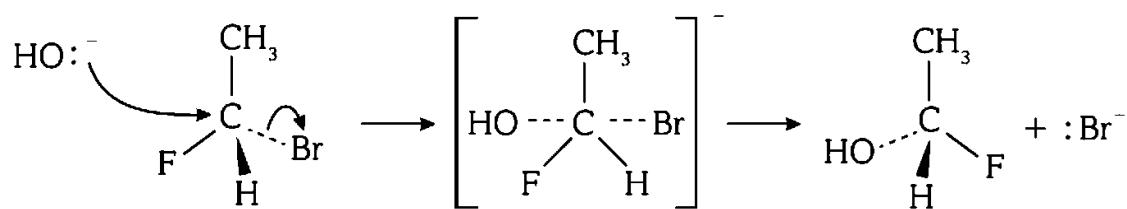
S = Substitution N = Nucleophilic 1 = unimolecular

Since a racemic mixture is formed, there will be no optical activity in product



S_N2 mechanism

No intermediates are formed, reaction proceeds in one step (via a transition state)



C-X bond breaks heterolytically and halogen, X leaves as an X^- ion

At the same time, nucleophile (OH^-) donates a pair of electrons to the $\delta+$ carbon atom, forming a new bond

If the original reactant was chiral then the opposite enantiomer would form

Notice how the nucleophile can only attack from the opposite direction of the C-Br bond- that is because bromine atom of the original halogenoalkane causes *steric hindrance*



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Addition to carbonyl compounds

15B: Carbonyl compounds

Students will be assessed on their ability to:

15.6	<p>understand the nomenclature of aldehydes and ketones and be able to draw their structural, displayed and skeletal formulae</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="background-color: #00aaff; color: white;">Structural Formula</th><th>Name</th><th>Molecular Formula</th></tr> </thead> <tbody> <tr> <td></td><td>methanal (also known as formaldehyde)</td><td>CH₂O</td></tr> <tr> <td></td><td>ethanal</td><td>C₂H₄O</td></tr> <tr> <td></td><td>propanal</td><td>C₃H₆O</td></tr> <tr> <td></td><td>propanone (also known as acetone)</td><td>C₃H₆O</td></tr> <tr> <td></td><td>pentan-2-one</td><td>C₅H₁₀O</td></tr> </tbody> </table>			Structural Formula	Name	Molecular Formula		methanal (also known as formaldehyde)	CH ₂ O		ethanal	C ₂ H ₄ O		propanal	C ₃ H ₆ O		propanone (also known as acetone)	C ₃ H ₆ O		pentan-2-one	C ₅ H ₁₀ O
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	pentan-2-one	C ₅ H ₁₀ O																			
	<p>Carbonyl compounds include aldehydes and ketones as they contain the carbonyl functional group (C=O)</p> <p>THE CARBONYL GROUP WILL ALWAYS HAVE AN H BONDED TO IT</p> <p>THE CARBONYL GROUP WILL BE BONDED TO 2 ALKYL GROUPS</p> <p>Nomenclature of aldehydes: Carbonyl group is always attached at the number 1 carbon of the chain General formula: RCHO</p> <p>Nomenclature of ketones: An alkyl group is present on each side of the carbonyl carbon of the chain General formula: RCOR</p>																				
15.7	<p>understand that aldehydes and ketones:</p> <ul style="list-style-type: none"> i do not form intermolecular hydrogen bonds and this affects their physical properties ii can form hydrogen bonds with water and this affects their solubility 																				
i	<p>Aldehydes and ketones have a dipole within their structure due to the O being more electronegative than C in the C=O bond</p> <p>This means that there are permanent dipole-permanent dipole forces in addition to London forces present between molecules</p> <p>However, there are no hydrogen bonds between molecules, so they have lower melting and boiling points than their respective alcohols</p>																				
ii	<p>Although they cannot form hydrogen bonds with their own molecules, they can form hydrogen bonds with water molecules</p> <p>This is due to the lone pair on the δ⁻ oxygen atom that forms hydrogen bonds with the δ⁺ hydrogen atom of water</p> <p>As a result, short chain aldehydes and ketones are soluble in water but longer chains are not soluble (as London forces predominate over hydrogen bonding and disrupts it)</p>																				

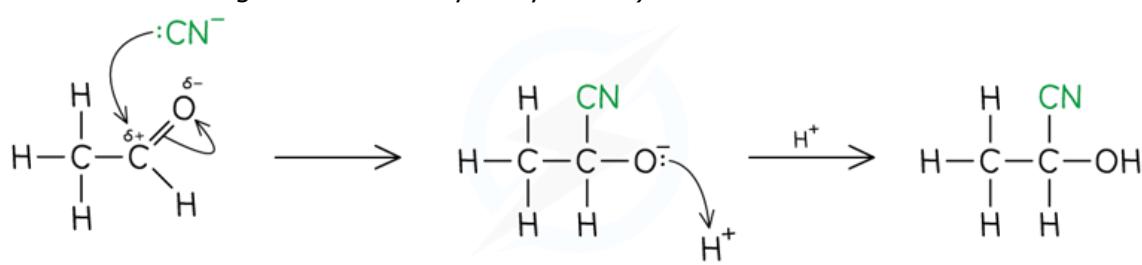
15.8	<p>understand the reactions of carbonyl compounds with:</p> <ul style="list-style-type: none"> i Fehling's or Benedict's solution, Tollens' reagent and acidified dichromate(VI) ions <i>In equations, the oxidising agent can be represented as [O].</i> ii lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether (ethoxyethane) <p><i>In equations, the reducing agent can be represented by [H].</i></p> <ul style="list-style-type: none"> iii HCN, in the presence of KCN, as a nucleophilic addition reaction, using curly arrows, relevant lone pairs, dipoles and evidence of optical activity to show the mechanism iv 2,4-dinitrophenylhydrazine (2,4-DNPH), as a qualitative test for the presence of a carbonyl group and to identify a carbonyl compound given data of the melting temperatures of derivatives <p><i>The equation for this reaction is not required.</i></p> <ul style="list-style-type: none"> v iodine in the presence of alkali (the iodoform test) 								
i	<p>Oxidation of aldehydes to form carboxylic acids (with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution or Tollens' reagent or Fehling's/Benedict's solution)</p> <div style="text-align: center; margin-top: 20px;"> <p style="margin-top: 10px;"> ALDEHYDE + OXIDISING AGENT $(\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4)$ → CARBOXYLIC ACID </p> <p style="font-size: small; margin-top: -20px;">Copyright © Save My Exams. All Rights Reserved</p> </div> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 10px;"> <thead> <tr> <th style="padding: 5px;">Reagent</th> <th style="padding: 5px;">Colour change</th> </tr> </thead> <tbody> <tr> <td style="padding: 5px;">Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate(VI))</td> <td style="padding: 5px;">Orange ($\text{Cr}_2\text{O}_7^{2-}$) to Green ($\text{Cr}^{3+}$)</td> </tr> <tr> <td style="padding: 5px;">Fehling's / Benedict's solution (alkaline solution containing Cu^{2+} ions)</td> <td style="padding: 5px;">Deep blue solution (CuSO_4^{2-}) to red precipitate (Cu_2O) Gradual color change from blue to green to yellow to red depending on the concentration of the ions present</td> </tr> <tr> <td style="padding: 5px;">Tollen's reagent (ammoniacal silver nitrate solution)</td> <td style="padding: 5px;">Colourless solution to silver mirror (silver precipitate)</td> </tr> </tbody> </table> <p style="margin-top: 10px;">!Note that Ketones do not normally undergo oxidation as they do not have a readily available hydrogen atom</p>	Reagent	Colour change	Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium dichromate(VI))	Orange ($\text{Cr}_2\text{O}_7^{2-}$) to Green (Cr^{3+})	Fehling's / Benedict's solution (alkaline solution containing Cu^{2+} ions)	Deep blue solution (CuSO_4^{2-}) to red precipitate (Cu_2O) Gradual color change from blue to green to yellow to red depending on the concentration of the ions present	Tollen's reagent (ammoniacal silver nitrate solution)	Colourless solution to silver mirror (silver precipitate)
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Tollen's reagent (ammoniacal silver nitrate solution)	Colourless solution to silver mirror (silver precipitate)								
ii	<p>Reduction (Reaction of both aldehyde and ketone with LiAlH_4 in <u>dry ether</u>) essential condition</p> <p>(Nucleophilic addition)</p> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 10px;"> <thead> <tr> <th style="padding: 5px;">Aldehydes are reduced to primary alcohols</th> <th style="padding: 5px;">Ketones are reduced to secondary alcohols</th> </tr> </thead> <tbody> <tr> <td style="padding: 5px;"> $\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{H}$ + 2[H] → $\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$ ALDEHYDE 1° ALCOHOL </td> <td style="padding: 5px;"> $\text{R}-\overset{\text{O}}{\underset{\text{R}}{\text{C}}}-\text{R}$ + 2[H] → $\text{R}-\overset{\text{H}}{\underset{\text{R}}{\text{C}}}-\text{OH}$ KETONE 2° ALCOHOL </td> </tr> </tbody> </table> <p style="margin-top: 10px;">Dry ether is used as a solvent because LiAlH_4 reacts with water to form hydrogen, making water not suitable</p>	Aldehydes are reduced to primary alcohols	Ketones are reduced to secondary alcohols	$\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{H}$ + 2[H] → $\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$ ALDEHYDE 1° ALCOHOL	$\text{R}-\overset{\text{O}}{\underset{\text{R}}{\text{C}}}-\text{R}$ + 2[H] → $\text{R}-\overset{\text{H}}{\underset{\text{R}}{\text{C}}}-\text{OH}$ KETONE 2° ALCOHOL				
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iii

Nucleophilic Addition

(Reaction of both aldehyde and ketone with HCN in the presence of aqueous alkaline solution containing KCN to form hydroxynitriles)

Hydroxynitriles
are produced!

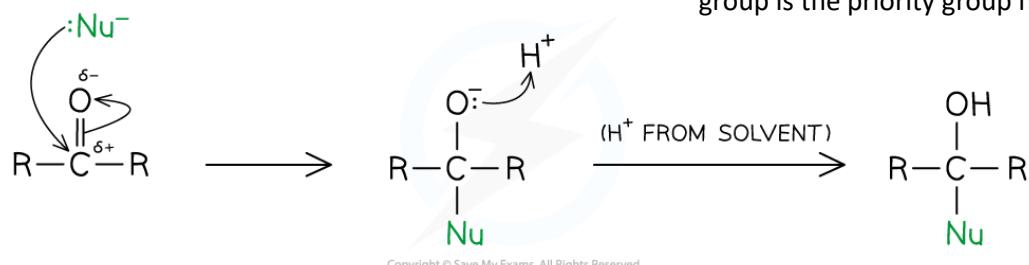


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In step 1, cyanide ion (nucleophile) attacks the carbonyl carbon to form a negatively charged intermediate

In step 2, the negatively charged oxygen atom in the intermediate quickly reacts with H^+ (either from HCN, water or dilute acid)

2-hydroxynitrile compound is formed
(Notice that -OH group is named with hydroxy instead of ending with -ol as the nitrile group is the priority group here)



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The carbonyl group (CHO) is planar which means in step 1, the cyanide ion (nucleophile) attacks equally from above and below the plane of carbonyl group. Hence, although the product contains a chiral centre, there are equal numbers of moles of the two enantiomers (laevorotatory and dextrorotatory) resulting in the product mixture having no optical activity (does not rotate plane of plane-polarised light)

iv

2,4-DNPH (Test for carbonyl group)

This reaction with 2,4-dinitrophenylhydrazine a.k.a. Brady's reagent can be used as a test for carbonyl compounds

Type of reaction: condensation

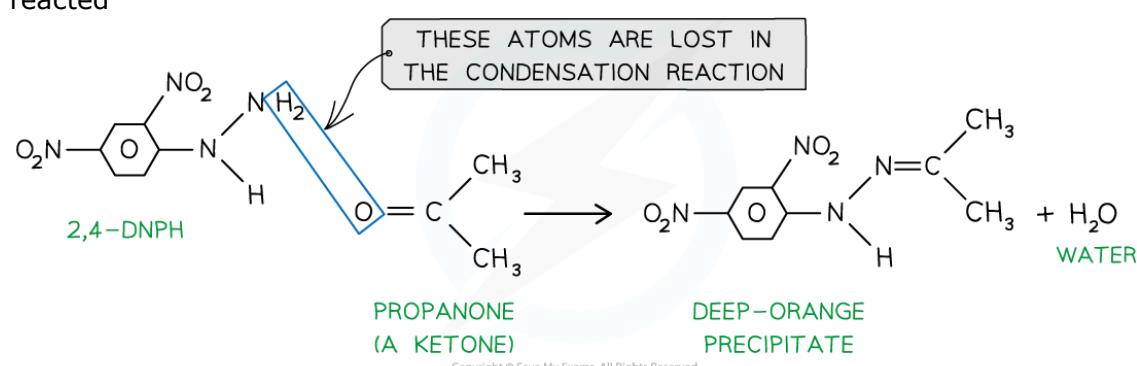
Positive observation: deep-orange precipitate

To deduce the carbonyl compound that reacted, the precipitates that form are recrystallised to purify them

Then, the melting point of the derivatives (precipitates that form) can be measured and compared to data book values to find out which specific ketone or aldehyde had reacted

A condensation reaction is a reaction in which two molecules join together and a small molecule, usually water, is eliminated

Note that carboxylic acids and esters do not give a positive result



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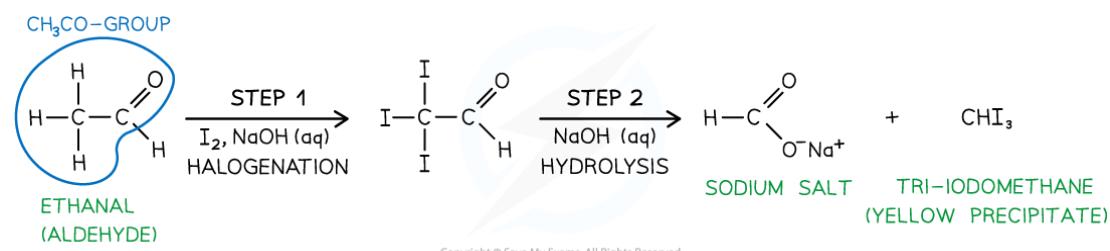
V***In alkaline conditions,*****Iodoform test with carbonyls (Test for CH₃CO group)**

When methyl ketones react with iodine and alkali, a yellow precipitate, (CHI₃) (Iodoform) tri-iodomethane is formed

(That includes ketones containing CH₃CO and this also means that ethanal is the only aldehyde that reacts to form iodoform)

Reagent: Iodine and NaOH solution (or any alkali)

Heat with reagents and then cool



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In halogenation step, all 3 H atoms in the CH₃ group are replaced with iodine atoms, forming a -I₃ group

In hydrolysis step, the intermediate is hydrolysed by an alkaline solution (NaOH) to form a sodium salt and a yellow precipitate

Overall reaction with aldehydes (only ethanal):



Overall reaction with ketones:



Where R is an alkyl group

Iodoform test with alcohols (Test for CH₃CH(OH))

When alcohols containing CH₃CH(OH) react with iodine and alkali, a yellow precipitate (iodoform) is formed

That includes all methyl secondary alcohols and this also means that ethanol is the only primary alcohol that reacts to from iodoform

Overall reaction is: CH₃CH(OH)R + 4I₂ + 6NaOH → RCOONa + CHI₃ + 5NaI + 5H₂O

In acidic conditions,

If propanone is reacted with iodine solution under acidic conditions, a different reaction occurs:



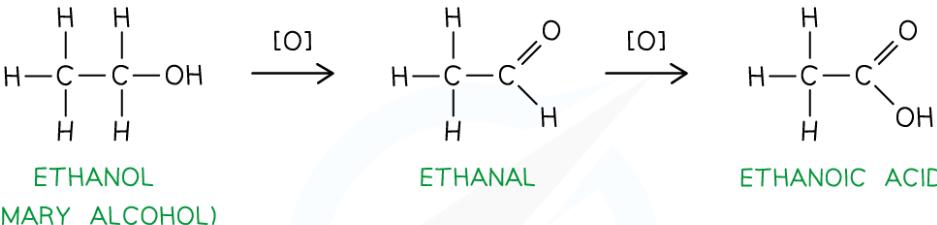
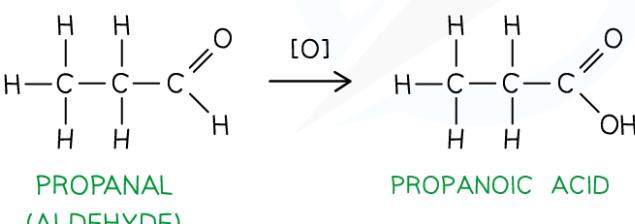
This reaction can also be used to study reaction kinetics as the brown colour of iodine fades to form a colourless liquid

Further suggested practical:

Reactions of aldehydes and ketones given in 15.8 i, iv and v

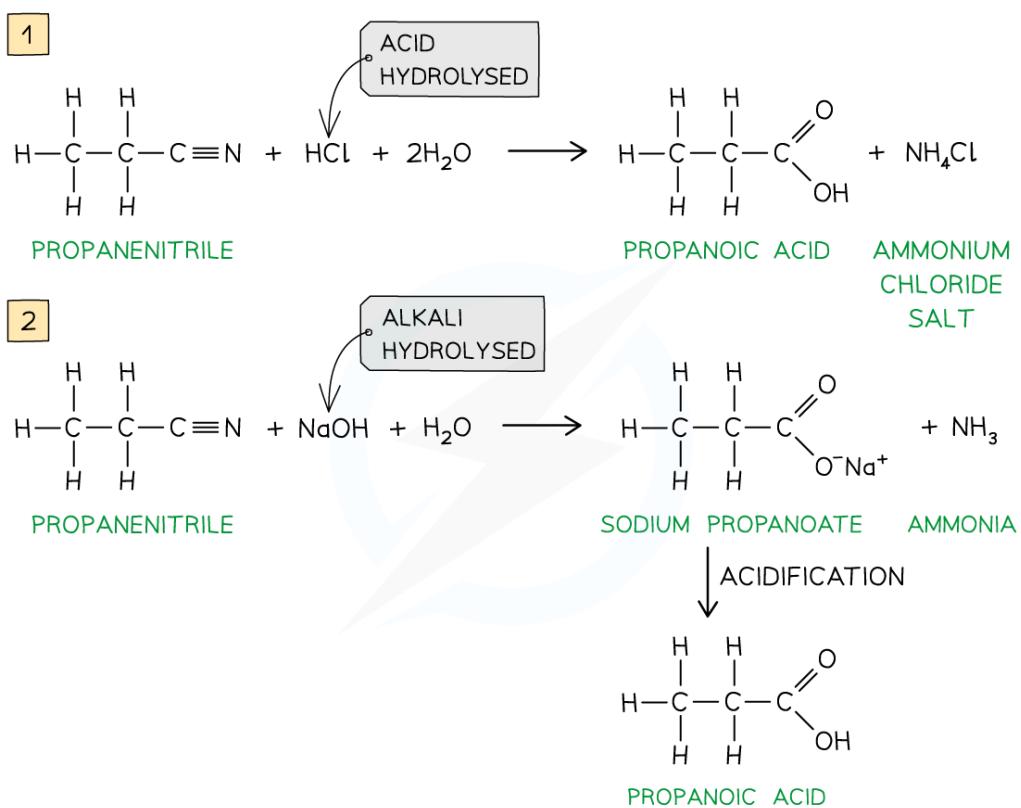
15C: Carboxylic acids

Students will be assessed on their ability to:

15.9	understand the nomenclature of carboxylic acids and be able to draw their structural, displayed and skeletal formulae														
	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; background-color: #0070C0; color: white;">Structural Formula</th> <th style="text-align: center; background-color: #0070C0; color: white;">Name</th> <th style="text-align: center; background-color: #0070C0; color: white;">Molecular Formula</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;"> $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{O}-\text{H} \end{array}$ </td><td>methanoic acid (also known as formic acid)</td><td>HCOOH</td></tr> <tr> <td style="text-align: center;"> $\begin{array}{c} \text{H} & \text{O} \\ & \parallel \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ & \text{H} \end{array}$ </td><td>ethanoic acid (also known as acetic acid)</td><td>CH₃COOH</td></tr> <tr> <td style="text-align: center;"> $\begin{array}{c} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{O}-\text{H} \\ & & \\ & \text{H} & \text{H} \end{array}$ </td><td>propanoic acid</td><td>CH₃CH₂COOH</td></tr> </tbody> </table>			Structural Formula	Name	Molecular Formula	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{O}-\text{H} \end{array}$	methanoic acid (also known as formic acid)	HCOOH	$\begin{array}{c} \text{H} & \text{O} \\ & \parallel \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ & \text{H} \end{array}$	ethanoic acid (also known as acetic acid)	CH ₃ COOH	$\begin{array}{c} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{O}-\text{H} \\ & & \\ & \text{H} & \text{H} \end{array}$	propanoic acid	CH ₃ CH ₂ COOH
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$\begin{array}{c} \text{H} & \text{H} & \text{O} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{O}-\text{H} \\ & & \\ & \text{H} & \text{H} \end{array}$	propanoic acid	CH ₃ CH ₂ COOH													
	<p>Carboxylic acid is a family of compounds that contain the carboxyl functional group (-COOH) General formula is: C_nH_{2n+1}COOH (or) RCOOH Nomenclature is: alkan + oic acid</p>														
15.10	understand that hydrogen bonding affects the physical properties of carboxylic acids, in relation to their boiling temperatures and solubility														
	<p>Carboxylic acids contain C=O and O-H groups which are polarized In addition to London and pd-pd forces, it is due to the OH group that it can form hydrogen bonds between its molecules, contributing to high melting and boiling points Additionally, it is due to the OH group (and C=O group) that it is soluble in water (shorter-chain carboxylic acids are soluble in water because they can form hydrogen bonds with water molecules) Solubility decreases as chain length increases as London forces predominate over the hydrogen bonds</p>														
15.11	understand that carboxylic acids can be prepared by the oxidation of alcohols or aldehydes and the hydrolysis of nitriles														
	<p>1. Oxidation of primary alcohols and aldehydes Heat under reflux with excess acidified K₂Cr₂O₇ (orange to green) or acidified KMnO₄ (purple to colourless) to form carboxylic acids</p> <p>1</p> <p style="text-align: center;">  ETHANOL (PRIMARY ALCOHOL) ETHANAL ETHANOIC ACID </p> <p>2</p> <p style="text-align: center;">  PROPANAL (ALDEHYDE) PROPANOIC ACID </p> <p style="text-align: right;"> [O] = ACIDIFIED K₂Cr₂O₇ OR ACIDIFIED KMnO₄ </p>														

2. Hydrolysis of nitriles

Heat under reflux nitriles with either dilute hydrochloric/sulfuric acid (or) dilute alkali, followed by acidification to form carboxylic acids



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15.12

understand the reactions of carboxylic acids with:

- i lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether (ethoxyethane)
- ii bases to produce salts
- iii phosphorus(V) chloride (phosphorus pentachloride)
- iv alcohols in the presence of an acid catalyst

i

Reduction with LiAlH_4

Carboxylic acids undergo reduction reaction with lithium tetrahydridoaluminate(III) in dry ether at room temperature to form primary alcohols

Type of reaction: reduction

Reagents: LiAlH_4 in dry ether

Conditions: room temperature and pressure

Reaction: $\text{CH}_3\text{CH}_2\text{COOH} (\text{l}) + 2[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} (\text{l}) + \text{H}_2\text{O} (\text{l})$

Addition of water at the end will destroy any excess LiAlH_4

ii

Reaction with bases

1. Reaction with metal oxides: acid + metal oxide \rightarrow metal salt + water
2. Reaction with alkalis: acid + alkali \rightarrow salt + water
3. Reaction with carbonates: acid + carbonate \rightarrow salt + carbon dioxide + water

iii

Reaction with PCl_5 (Test for carboxylic acids)

Carboxylic acids react with solid PCl_5 to form an acyl chloride (functional group COCl)

Reaction: $\text{CH}_3\text{CH}_2\text{COOH} (\text{l}) + \text{PCl}_5 (\text{s}) \rightarrow \text{CH}_3\text{CH}_2\text{COCl} (\text{l}) + \text{POCl}_3 (\text{l}) + \text{HCl} (\text{g})$

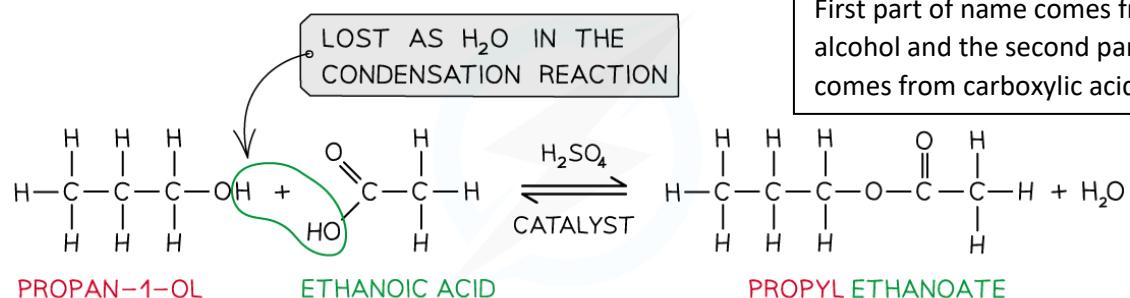
This is also used as a test for carboxylic acids (misty fumes observed)

iv

Reaction with alcohols (esterification)

Carboxylic acids react with alcohols in the presence of an acid catalyst (concentrated H_2SO_4) to form esters and water (Esters are compounds with -COOR functional group and characterized by their sweet and fruity smell)

Type of reaction: condensation reaction



Nomenclature of esters:

First part of name comes from alcohol and the second part comes from carboxylic acid

Further suggested practicals:

- i solubility of a range of carboxylic acids, aldehydes and ketones
- ii preparation of carboxylic acids by the oxidation of alcohols and aldehydes
- iii reactions of carboxylic acids given in 15.12 ii, iii and iv

15D: Carboxylic acid derivatives

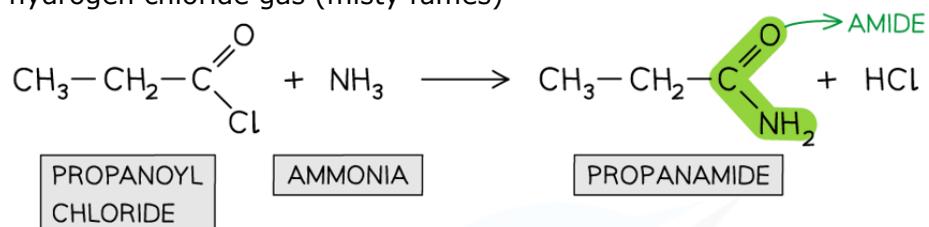
Students will be assessed on their ability to:

15.13	<p>understand the nomenclature of acyl chlorides and esters and be able to draw their structural, displayed and skeletal formulae</p>			
	 CARBOXYLIC ACID	 ACYL CHLORIDE	 ACID ANHYDRIDE	<p>Acyl chlorides are derivatives of carboxylic acids formed by the substitution of the -OH group by a Cl atom Nomenclature is: alkan + oyl chloride</p>
	 ETHANOIC ACID	 ETHANOYL CHLORIDE	 ETHANOIC ANHYDRIDE	<p>Acid anhydrides are also derivatives of carboxylic acids formed by substitution of the -OH group by an alkanate Nomenclature is: alkan+ oic anhydride</p>
	<p>They undergo <i>nucleophilic addition-elimination reactions</i> where the nucleophilic addition of a small molecule across the C=O bond takes place followed by elimination of a small molecule (all reactions below are <i>nucleophilic addition-elimination</i>)</p>			
15.14	<p>understand the reactions of acyl chlorides with:</p> <ul style="list-style-type: none"> i water ii alcohols iii concentrated ammonia iv amines 			
i	<p>Hydrolysis Acyl chlorides react vigorously with cold water, forming a carboxylic acid and hydrogen chloride gas (misty fumes)</p>			
	 PROPANOYL CHLORIDE	$\text{CH}_3\text{---CH}_2\text{---C}(=\text{O})\text{Cl} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{---CH}_2\text{---C}(=\text{O})\text{---OH} + \text{HCl}$	 PROPANOIC ACID	
ii	<p>Reaction with Alcohols Acyl chlorides react readily with alcohols, forming an ester and hydrogen chloride gas (misty fumes) Takes place at room temperature</p>			
	 PROPANOYL CHLORIDE	$\text{CH}_3\text{---CH}_2\text{---C}(=\text{O})\text{Cl} + \text{CH}_3\text{---CH}_2\text{---OH} \longrightarrow \text{CH}_3\text{---CH}_2\text{---C}(=\text{O})\text{---O---CH}_2\text{---CH}_3 + \text{HCl}$	 ETHYL PROPANOATE	

iii

Reaction with concentrated ammonia

Acyl chlorides react readily with concentrated ammonia, forming an amide and hydrogen chloride gas (misty fumes)



Hang on! It's not done- since the reactant is a base and the product is an acidic gas:

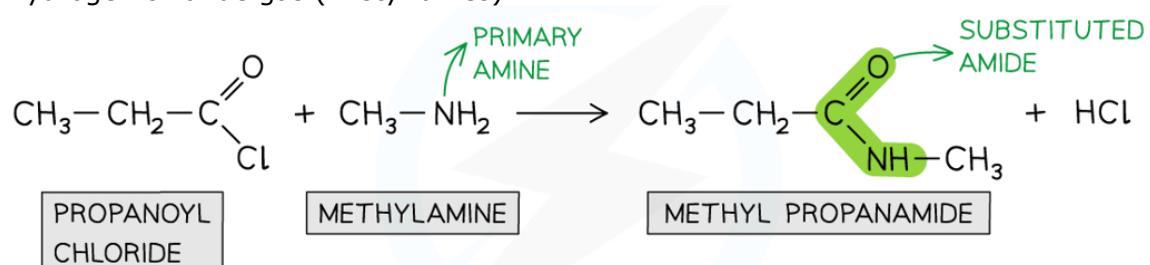


The overall equation is: $\text{CH}_3\text{COCl} + \text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{NH}_4\text{Cl}$

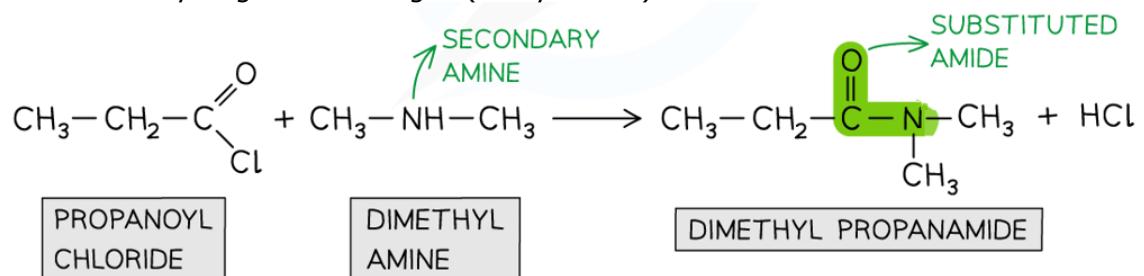
iv

Reaction with amines

Acyl chlorides react with primary amines (RNH_2), forming an N-substituted amide and hydrogen chloride gas (misty fumes)



Acyl chlorides react with secondary amines (R_2NH), forming an N,N-disubstituted amide and hydrogen chloride gas (misty fumes)



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15.15

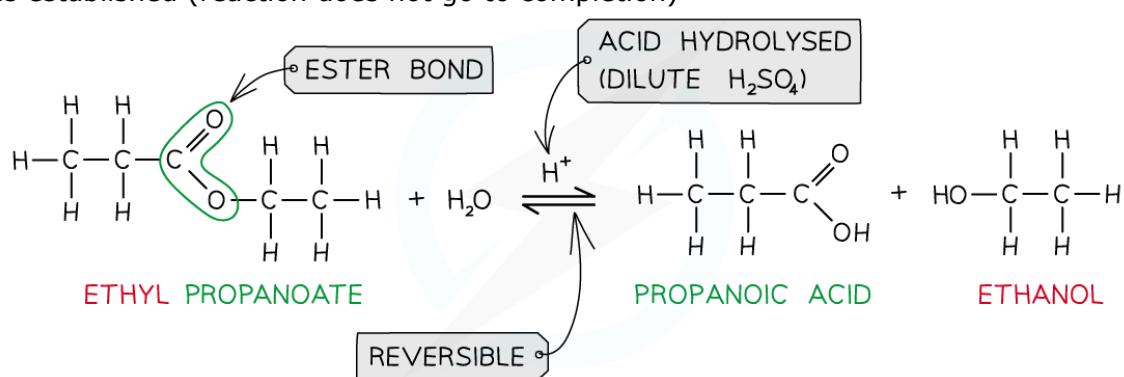
understand the hydrolysis reactions of esters, in acidic and alkaline solution

Esters are colourless liquids with a fruity smell that have low melting and boiling points and are insoluble in water (no hydrogen bonds)

Recall that the first part of an ester's name is from the alcohol and the last part comes from the carboxylic acid

Hydrolysis in acidic solution

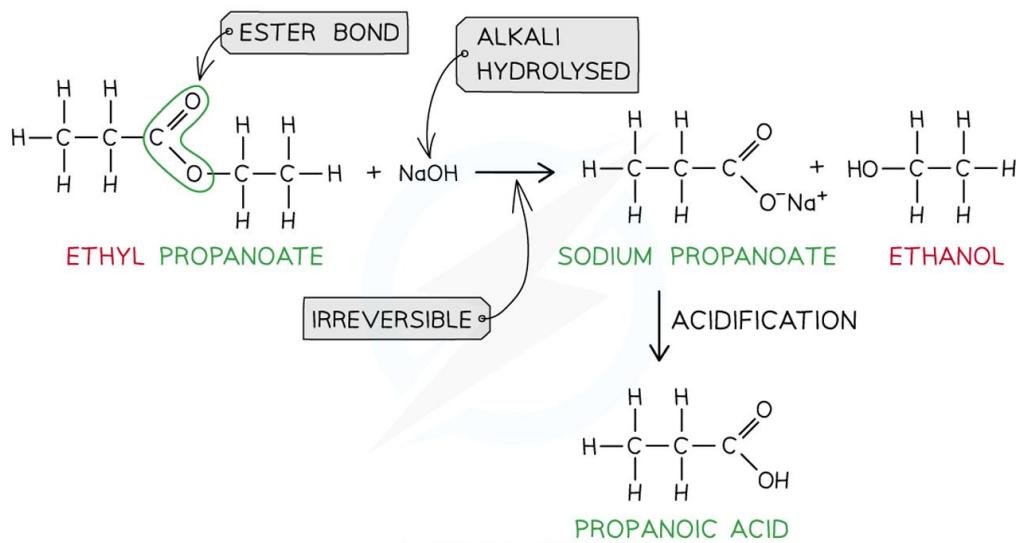
When an ester is heated under reflux with dilute acid (H_2SO_4), an equilibrium mixture is established (reaction does not go to completion)



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Hydrolysis in alkaline solution

In contrast with the above reaction, heating the ester under reflux with dilute alkali (NaOH) is an irreversible reaction (reaction goes to completion)
Alcohol and carboxylate salt is produced which can be converted into carboxylic acid with a dilute acid



15.16

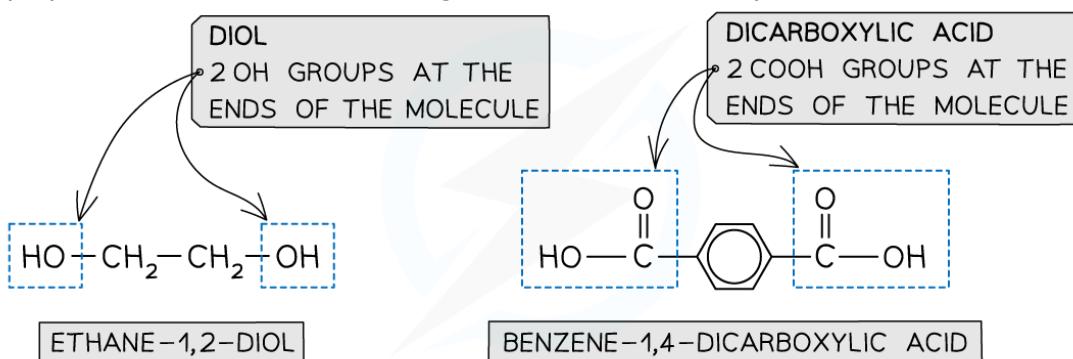
understand how polyesters, such as terylene, are formed by condensation polymerisation reactions

Addition polymerization has been covered in your AS studies, now we will look at:
Condensation Polymerisation

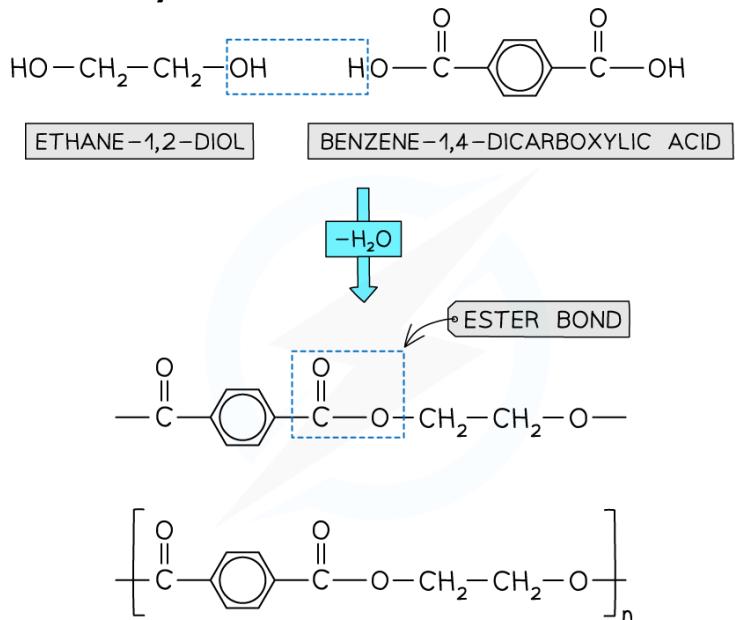
- is the formation of a polymer by the reaction of two different monomers, with the elimination of a small molecule (usually water or hydrogen chloride)
- Condensation polymers can be identified because the monomers are linked by ester or amide bonds

Formation of polyesters

A polyester is formed from reacting a diol with a dicarboxylic acid



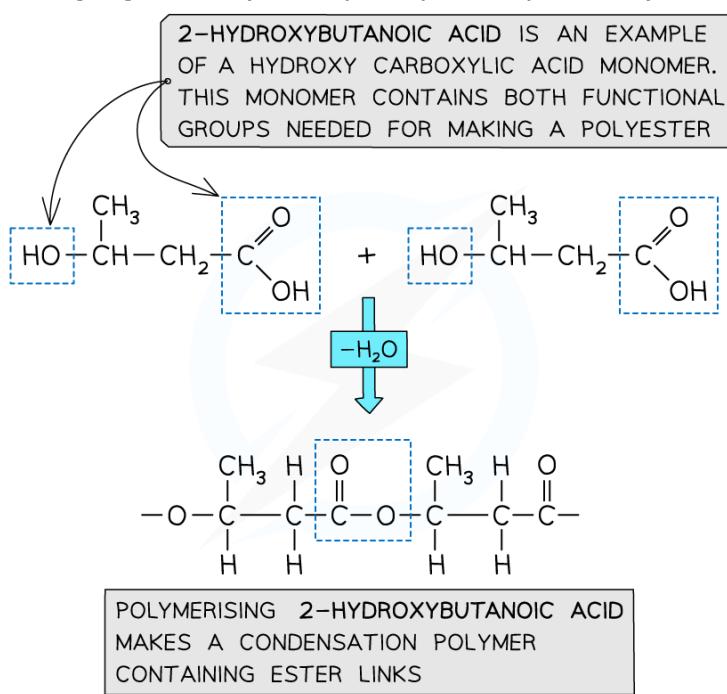
Formation of Terylene



THE POLYMER STRUCTURE FOR POLY(ETHYLENE TEREPHTHALATE) (PET)

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Formation of polyesters (from hydroxycarboxylic acids)



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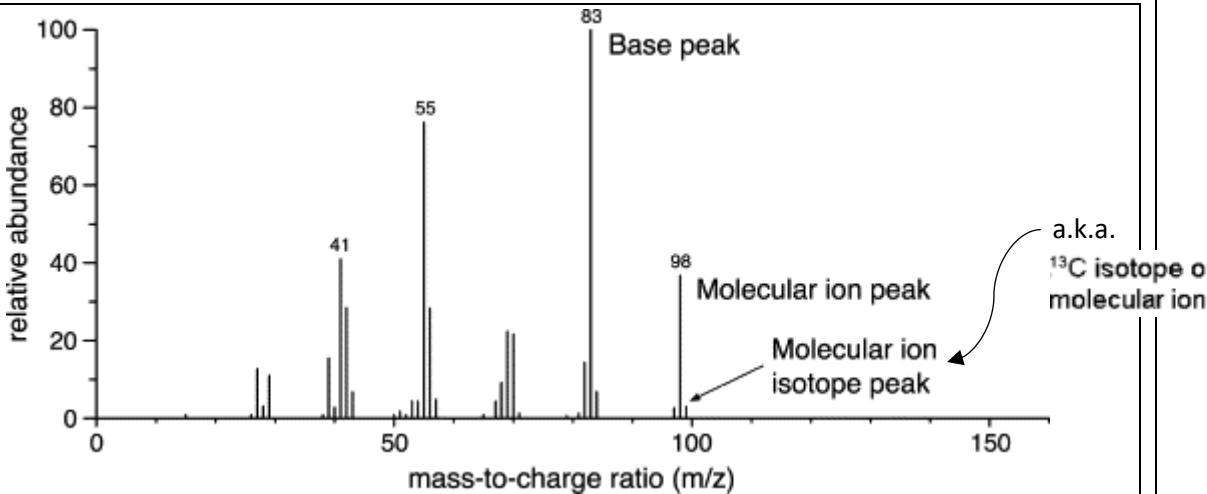
Further suggested practicals:

- demonstration of the reactions of ethanoyl chloride given in 15.14 i, ii and iii
- the preparation of esters such as ethyl ethanoate as a solvent or a pineapple flavouring
- hydrolysis of an ester

15E: Spectroscopy and chromatography

Knowledge of the concepts introduced in Unit 2, Topic 10D: Mass spectra and IR will be assumed and extended in this topic

Students will be assessed on their ability to:

15.17	<p>be able to use data from mass spectra to:</p> <ul style="list-style-type: none"> i suggest possible structures of a simple organic compound given accurate relative molecular masses ii calculate the accurate relative molecular mass of a compound, given accurate relative atomic masses to four decimal places 															
i Refer to 2.6 Refer to 10.21	<p>At AS level, we have learned that we can use MS (mass spectrometry) to determine:</p> <ul style="list-style-type: none"> - A_r (relative atomic mass) from isotopic abundances $A_r = \frac{(relative\ abundance_{isotope\ 1} \times mass_{isotope\ 1}) + (relative\ abundance_{isotope\ 2} \times mass_{isotope\ 2}) + \dots}{100}$ <ul style="list-style-type: none"> - Possible molecular formula of organic compounds using the m/z of the molecular ion peak and its structure using fragmentation patterns 															
Remember! <p>During AS, we also learned about IR (infrared spectroscopy) to deduce functional groups present in organic compounds</p> HRMS determines the M_r but not always its structure as it is possible for two different structures to have the same accurate M_r value. <p>Nonetheless, its structure can be deduced from fragmentation patterns</p>	<p>At A2 level, we will learn more about mass spectrometry and how to determine:</p> <ul style="list-style-type: none"> - The molecular formula of an organic compound (although not always its structure) from a precise (4 or more d.p.) relative molecular mass obtained from high resolution mass spectrometry (HRMS) and then comparing it with the molecular formula that we can work out using accurate relative atomic mass <p>A compound is found to have an M_r value of 84.0573. Which of these is the correct structure for the compound?</p> <p>$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHO}$</p> <p>Now we work out each M_r to 4 decimal places using accurate A_r information which will be provided in the exam, just like the following table</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>ELEMENT</th> <th>SYMBOL</th> <th>ACCURATE ATOMIC MASS</th> </tr> </thead> <tbody> <tr> <td>hydrogen</td> <td>H</td> <td>1.0078</td> </tr> <tr> <td>carbon</td> <td>C</td> <td>12.0000</td> </tr> <tr> <td>nitrogen</td> <td>N</td> <td>14.0031</td> </tr> <tr> <td>oxygen</td> <td>O</td> <td>15.9949</td> </tr> </tbody> </table> <p>$M_r (\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3) = 84.0936$</p> <p>$M_r (\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHO}) = 84.0573$ (this value is the same as the given M_r value)</p> <p>Hence, compound is $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$</p>	ELEMENT	SYMBOL	ACCURATE ATOMIC MASS	hydrogen	H	1.0078	carbon	C	12.0000	nitrogen	N	14.0031	oxygen	O	15.9949
ELEMENT	SYMBOL	ACCURATE ATOMIC MASS														
hydrogen	H	1.0078														
carbon	C	12.0000														
nitrogen	N	14.0031														
oxygen	O	15.9949														

15.18

understand that carbon-13, (^{13}C) NMR spectroscopy provides information about the positions of ^{13}C atoms in a molecule

Remember! ^{12}C and ^2H atoms will NOT show up on NMR, only ^{13}C and ^1H will!
(Notice how ^{13}C and ^1H have an odd number of nucleons- that means it has a residual spin which creates a magnetic field around it that can interact with an external magnetic field)

At A2 level, you will also learn about a third major analysing technique for organic compounds in addition to MS (*mass spectroscopy*) and IR (*infrared spectroscopy*)

- It is called the **NMR spectroscopy** (*Nuclear Magnetic Resonance Spectroscopy*) which is used to determine the structure of an organic compound by providing information on the number and types of carbon atoms present
- It **detects** the magnetic properties of the **^{13}C isotope** (which has an odd number of particles in its nucleus) to reveal the chemical environment of each carbon atom, appearing as peaks on a spectrum
- The position of these peaks (chemical shift) indicates the type of carbon, while the number of signals shows the number of unique carbon environments

Some short key points on *how an NMR spectroscopy works*

- Protons and neutrons have *opposite spins*
- Nuclei have either an even or an odd number of nucleons (*if even, spins cancel out and if odd, residual spin exists*)
- *Residual spin causes a mini magnetic field* (makes nuclei act like a magnet)
- In absence of external magnetic field, these nuclei are randomly oriented
- If placed in an external magnetic field, these *nuclei either line up parallel to it (lower energy state) or oppose it (higher energy state)*
- This results in an energy difference between these two states of a nucleus
- This means the nuclei can absorb EM radiation (i.e. radio waves)
- When nuclei are bombarded with EM radiation, nuclei in lower energy state absorb this energy and excites to higher energy state and eventually de-excites and releases energy which is detected by the spectrometer

The nuclei of two adjacent atoms in a molecule influence each other and electrons can also influence the amount of radiation absorbed by a particular nuclei in a molecule and these are detected as signals at different frequencies

Vertical axis: absorption (no units)

Horizontal axis: chemical shift (ppm)

Some key points on interpreting the spectrum produced:

- **Each distinct carbon environment in a molecule** gives a **unique signal** in the ^{13}C NMR spectrum
- The **chemical shift** (in ppm) tells you about the **chemical environment** of that carbon (i.e. whether it's part of a carbonyl, alkene, aromatic ring, alkane)
- The **number of signals** indicates number of **unique carbon environments** (NOT the total number of carbon atoms as symmetry can reduce the number of signals)

For an atom to show, it must have an odd number of nucleons which means Carbon-12 atoms won't appear, but only Carbon-13 atoms will

Most solvents contain carbon and hydrogen atoms so they will interfere with the results so **CDCl_3** is used which does not interfere in any way

All samples are measured against a reference compound—**Tetramethylsilane** (TMS)

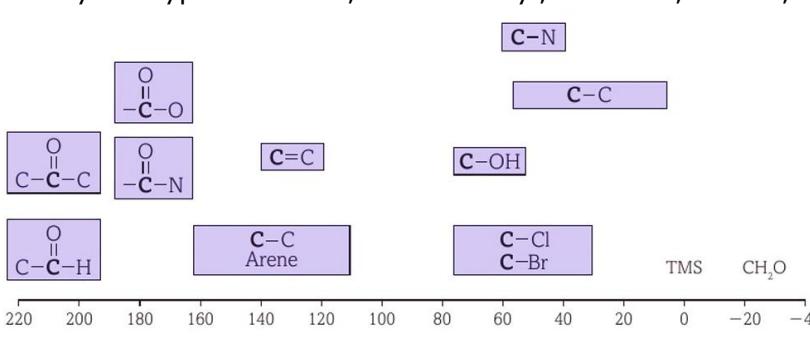
- TMS has a chemical shift of 0 ppm
- Not toxic
- Does not react with sample
- Easily separated from sample due to its low boiling point

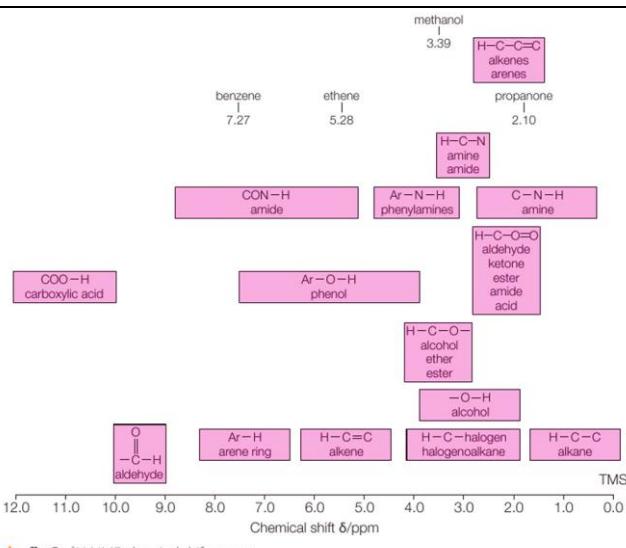
Extra knowledge!

The solvents of choice normally are **tetrachloromethane (CCl_4)** or **deuterated trichloromethane (CDCl_3)** as CCl_4 contains no hydrogen atoms at all and CDCl_3 contains deuterium (^2H) whose *nucleon number is even*

Hence, deuterium atoms do not have **nuclear spin** and hence do not interact with the external magnetic field used in NMR spectroscopy

Absorptions from deuterium atoms **will not be detected** and hence will not produce a peak

15.19	<p>be able to use data from ^{13}C NMR spectroscopy to:</p> <ul style="list-style-type: none"> i predict the different environments for carbon atoms present in a molecule, given values of chemical shift, δ ii justify the number of peaks present in a ^{13}C NMR spectrum in terms of the number of carbon atoms in different environments
<p>i</p> <p>Chemical shift chart is given in the exam!</p>	<p>To use ^{13}C NMR chemical shift data (δ) to predict carbon environments:</p> <ol style="list-style-type: none"> 1. Analyze the number of unique signals and their corresponding chemical shift values as each unique signal indicates a distinct carbon environment 2. Compare the chemical shift (δ) values with a reference chemical shift chart from the data booklet <p>It helps identify the type of carbon, such as alkyl, aromatic, alkene, or carbonyl</p>  <p>▲ fig B ^{13}C NMR chemical shift ranges.</p>
<p>ii</p>	<p>We need to justify the number of peaks present for a particular compound as some factors such as symmetry can lead to fewer peaks being produced than the actual number of carbon atoms</p> <p>To justify peak count:</p> <ol style="list-style-type: none"> 1. Determine the number of peaks 2. Count the number of individual carbon atoms that would be in that unique chemical environment 3. Account for planes of symmetry and/or bond rotations
15.20	<p>be able to use both low and high resolution proton NMR spectroscopy to:</p> <ul style="list-style-type: none"> i predict the different types of proton present in a molecule, given values of chemical shift, δ ii relate relative peak areas, or ratio number of protons, to the relative numbers of ^1H atoms in different environments iii deduce the splitting patterns of adjacent, non-equivalent protons using the $(n+1)$ rule and hence suggest the possible structures for a molecule iv predict the chemical shifts and splitting patterns of the ^1H atoms in a given molecule
<p>i</p>	<p>To use ^1H proton NMR spectroscopy to predict proton environments:</p> <ol style="list-style-type: none"> 1. Analyze the number of unique signals and their corresponding chemical shift values as each signal indicates a distinct proton environment 2. Compare the chemical shift (δ) values with a reference chemical shift chart <p>It helps identify the type of proton, such as alkyl or aromatic</p> <ol style="list-style-type: none"> 3. This is where low and high resolution proton NMR differs: Low-resolution spectra only shows distinct chemical shift regions for different proton environments while High-resolution spectra also provides splitting patterns that reveals the number of adjacent, non-equivalent protons using the $n+1$ rule



▲ fig C ^1H NMR chemical shift ranges.

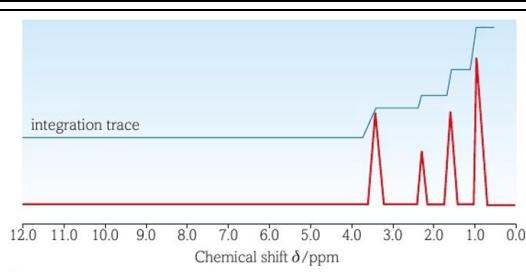
ii The relative **areas under the peaks**, or the ratio of the number of protons, in both low and high resolution proton NMR spectra **are directly proportional to the relative numbers of (^1H) hydrogen atoms** in different chemical environments

- Usually, a number beside the peak indicates the relative area of the peak
- Or, the relative area can be shown by an integration trace

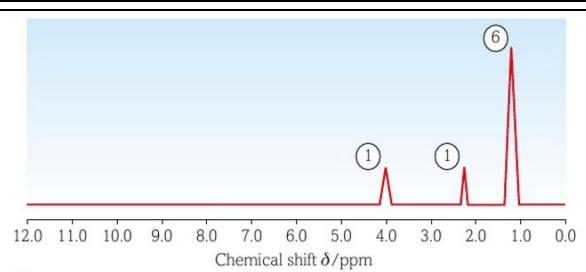
NOTE! That this is not the case for ^{13}C NMR spectrum

In ^{13}C NMR, **peak area is generally not directly proportional to the number of carbon atoms** and cannot be used for reliable integration, unlike in ^1H NMR

Instead, the intensity or height of a ^{13}C peak is affected by factors such as relaxation times (which are long for ^{13}C nuclei) and the presence of decoupling or DEPT experiments, leading to random peak heights (which you do not need to know)



▲ fig A The low resolution ^1H NMR spectrum of propan-1-ol.



▲ fig B The low resolution ^1H NMR spectrum of propan-2-ol.

iii To deduce splitting patterns in high resolution spectra:

Number of adjacent protons (n)	Splitting pattern using the $n+1$ rule the peak will split into...	Relative intensities in splitting pattern	Shape
0	1, singlet	1	
1	2, doublet	1:1	
2	3, triplet	1:2:1	
3	4, quartet	1:3:3:1	

Apply the **(n+1) rule** where 'n' is the **number of adjacent, non-equivalent protons on the carbon atom immediately next to** the carbon atom producing the signal, to predict the number of peaks the signal will split into (singlet, doublet, triplet, etc)

In a high-resolution spectrum, the splitting of a signal (spin-spin coupling) occurs due to the magnetic field of adjacent, non-equivalent protons

By combining information from the number of signals, integration, and splitting patterns, you can identify the types of functional groups and their connectivity, allowing you to suggest possible molecular structures

iv	<p>So we are doing the opposite here now- predicting the ^1H NMR spectrum including its chemical shifts and splitting patterns from a given molecule</p> <p>To predict this:</p> <ol style="list-style-type: none"> 1. Identify distinct proton environments to determine the number of signals that will show up on the spectrum 2. Identify the number of protons to determine their relative intensities on the spectrum 3. Use the chemical shift table from the data booklet to determine the position (i.e. chemical shift value) of each signal 4. Count the number of adjacent, non-equivalent protons and use the n+1 rule to identify the splitting pattern and the number of sub-peaks (singlet, etc)
Try it out! 2018 June U4 Q-12(d)	<p>*(d) Compare the high resolution proton nmr spectrum of ethyl ethanoate, $\text{CH}_3\text{COOC}_2\text{H}_5$, with that of methyl propanoate, $\text{C}_2\text{H}_5\text{COOCH}_3$. You should include</p> <ul style="list-style-type: none"> • two similarities and two differences • information from the Data Booklet, quoting chemical shift ranges for all the peaks • an explanation for one splitting pattern of your choice. <p style="text-align: right;">(5)</p>

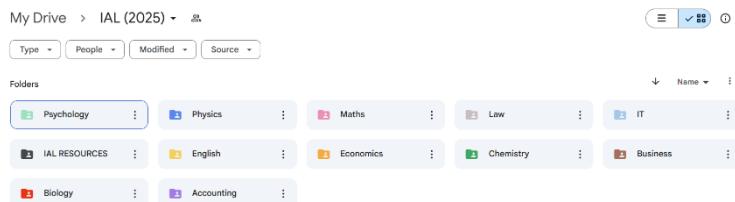
15.21	<p>know that chromatography separates components of a mixture using a mobile phase and a stationary phase</p> <p>Chromatography</p> <ul style="list-style-type: none"> - separates mixture components by having a liquid or gas mobile phase carry the mixture through a stationary phase - The stationary phase remains fixed in place while the mobile phase carries the components of the mixture through the medium being used <p>Components separate based on their differing affinities (strength of attraction) for the stationary phase and solubilities in the mobile phase, causing them to travel at different speeds</p> <ul style="list-style-type: none"> - Components that are <i>more soluble in the mobile phase or have weaker interactions with the stationary phase</i> move faster and are observed first - Components that are <i>less soluble in the mobile phase or have stronger interactions with the stationary phase</i> move slower and are observed last <p>Types of Chromatography</p> <ol style="list-style-type: none"> 1. Paper chromatography <p>In paper chromatography, the stationary phase is the water trapped in the fibres of paper and the mobile phase is the solvent</p> <ol style="list-style-type: none"> 2. Thin-layer chromatography (TLC) <p>In TLC, the stationary phase is a sheet of glass or plastic coated in a thin layer of alumini or silica while the mobile phase is either a polar (water or alcohol) or non-polar solvent (alkanes)</p> <ol style="list-style-type: none"> 3. Column chromatography (CC) <ol style="list-style-type: none"> i) gas chromatography (GC) ii) high performance liquid chromatography (HPLC) <p>All these chromatography techniques make use of the principle that components in a mixture when dissolved in a liquid (mobile phase), will flow through another material (stationary phase) at varying rates</p> <p>The rate of separation depends on how the components in the mixture interact with the stationary phase (their retention) and how soluble they are in the mobile phase</p> <table border="1"> <thead> <tr> <th>Chromatography technique</th><th>Stationary phase</th><th>Mobile Phase</th></tr> </thead> <tbody> <tr> <td>Thin-layer (TLC)</td><td>Solid silica on a plastic or glass plate</td><td>Liquid solvent, e.g. water or organic</td></tr> <tr> <td>Column (CC)</td><td>Solid silica</td><td>Liquid solvent, e.g. water or organic</td></tr> <tr> <td>Gas – Liquid (GLC)</td><td>Microscopic liquid film on a solid support</td><td>Inert carrier gas, e.g. nitrogen</td></tr> </tbody> </table>	Chromatography technique	Stationary phase	Mobile Phase	Thin-layer (TLC)	Solid silica on a plastic or glass plate	Liquid solvent, e.g. water or organic	Column (CC)	Solid silica	Liquid solvent, e.g. water or organic	Gas – Liquid (GLC)	Microscopic liquid film on a solid support	Inert carrier gas, e.g. nitrogen
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Column (CC)	Solid silica	Liquid solvent, e.g. water or organic											
Gas – Liquid (GLC)	Microscopic liquid film on a solid support	Inert carrier gas, e.g. nitrogen											
15.22	<p>be able to calculate R_f values from one-way chromatograms in paper and thin-layer chromatography (TLC) and understand reasons for differences in R_f values</p> <p>Remember that R_f value has no units and is always between 0 and 1</p> <p>To calculate a Retardation (or) Retention Factor (R_f) value:</p> <ul style="list-style-type: none"> - Divide the distance traveled by the substance from the baseline by the distance traveled by the solvent front, also from the baseline $R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$ <ul style="list-style-type: none"> - Factors such as the polarity of the mobile phase, the nature of the stationary phase (paper or TLC plate), temperature, and solvent concentration influence R_f values <p>More polar compounds will have a stronger affinity for a polar stationary phase (like silica gel in TLC) and will adhere to it more strongly, resulting in lower R_f values</p> <p>A more polar solvent will have a stronger interaction with a polar stationary phase and will more easily overcome the compound's affinity for the stationary phase, allowing the compound to travel further and have a higher R_f value</p>												

	<ul style="list-style-type: none"> - A higher R_f value indicates the substance is less polar or interacts less with the stationary phase, moving more freely with the solvent 				
15.23	<p>know that high-performance liquid chromatography, HPLC, and gas chromatography, GC, are types of column chromatography that separate substances because of different retention times in the column and may be used in conjunction with mass spectrometry, in applications such as forensics or drug testing in sport</p>				
	<p>Both HPLC and GC are types of column chromatography that separate substances based on their different retention times in the column due to their varied interactions with the stationary and mobile phases</p> <p>These techniques are often coupled with MS to be used in forensic science and drug testing in sports to analyze compounds in samples</p> <p>HPLC vs GC</p> <table border="1"> <tr> <td>In HPLC,</td> <td>In GC,</td> </tr> <tr> <td> <ul style="list-style-type: none"> - Mobile phase is a non-polar liquid (hexane, heptane) - Stationary phase is polar and a solid (usually silica) - HPLC operates at much lower temperatures (around 20-40°C) - HPLC is suitable for non-volatile and thermally unstable compounds (such as proteins and amino acids) </td> <td> <ul style="list-style-type: none"> - Mobile phase is an inert carrier gas (helium, nitrogen, argon) - Stationary phase is a liquid (in the column) - GC requires high temperatures (150-300°C or more) to vaporize samples - GC is best for volatile and thermally stable compounds </td> </tr> </table> <p>(c) Trimethylamine is a major air pollutant originating from food waste, farm animals and vehicle exhausts. Trimethylamine levels need to be monitored as it can easily be absorbed through human skin.</p> <p>Gas chromatography (GC) can be used to measure the level of trimethylamine in air, using the apparatus shown in the diagram.</p> <p>(i) Briefly describe how trimethylamine will be separated from other chemicals present in the sample of air. (2)</p> <p>Inert gas carries samples through the column / the gas is a mobile phase</p> <p>Compounds are attracted to the contents of the column / the contents in the column are the stationary phase</p> <p>Compounds that are strongly attracted to the stationary phase take longer to pass through the column / compounds that are not attracted to the stationary phase take less time to pass through the column</p> <p>(ii) High-performance liquid chromatography (HPLC) is used to measure levels of trimethylamine and trimethylamine N-oxide in blood and urine. Label the x-axis on the chromatogram. (1)</p> <p>(iii) Name the analytical technique that can be used with either GC or HPLC to identify the compound responsible for each peak. (1)</p> <p>Mass spectrometry</p>	In HPLC,	In GC,	<ul style="list-style-type: none"> - Mobile phase is a non-polar liquid (hexane, heptane) - Stationary phase is polar and a solid (usually silica) - HPLC operates at much lower temperatures (around 20-40°C) - HPLC is suitable for non-volatile and thermally unstable compounds (such as proteins and amino acids) 	<ul style="list-style-type: none"> - Mobile phase is an inert carrier gas (helium, nitrogen, argon) - Stationary phase is a liquid (in the column) - GC requires high temperatures (150-300°C or more) to vaporize samples - GC is best for volatile and thermally stable compounds
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